

Washing Clean-up of Cu(II)-phenanthrene Co-contaminated Soil by Surfactants

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Abstract

In this paper, the feasibility of mixed anionic-nonionic surfactants to remove copper (II) (Cu)-phenanthrene (Phen) co-contaminants from soil was investigated using batch washing method. The comparison on the removal of contaminants using single and mixed surfactants was conducted. The capability of a nonionic surfactant, octyl phenol polyethylene ether (TX100), to wash Phen out from soil was much larger than that to Cu while an anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), was more capable to remove Cu efficiently. The mixed SDBS-TX100 exhibited significant capability to sweep the co-contaminants out from soil. The overall removal efficiencies of co-contaminants by mixed surfactant were larger than those by single surfactants. The results indicated that mixed anionic-nonionic surfactant could be applied in the remediation of soils contaminated with both organics and heavy metals.

Keywords

Ex Situ Washing; Co-Contamination; Copper (II); Phenanthrene; Surfactant

Introduction

The pollutants in soil environment mainly include heavy metals, organic pollutants, radioactive substances, excessive nitrogen (N), phosphorus (P) and pathogenic bacteria etc., which threat food security and human survival environments. One type of pollutants often exists with the other type(s) of pollutants in the soils, i.e. co-contamination, resulting in complex effects on the ecological environment. Among them, the co-contamination of heavy metals with toxic organic pollutants has become one common phenomenon in soil environment. (Amaraneni 2006, Tang et al. 2010).

Surfactant washing/flushing technology has been popularly used in the clean-up of the soils contaminated with organics (Ghosh & Tick, 2013) while chelant washing/flushing one in the remediation of heavy metal-contaminated soils (Zhang & Tsang 2013), due to high efficiency and short cycle derived from the strong interactions between organic pollutant molecules and surfactant micelles, and between heavy metal ions and chelant molecules (Zhang et al. 2008). Therefore, as for the remediation of soils contaminated with both heavy metals and organics, surfactant and chelant are simultaneously or sequentially used in flushing/washing procedures in order to sweep co-contaminants out from soils (Khodadoust et al. 2005, Ehsan et al. 2006, Zhang et al. 2007, Yuan et al. 2010, Rivero-Huguet & Marshall 2011, Wen & Marshall 2011, Cao et al. 2013). However, their joint application was limited due to the less biodegradability of conventional chelants, such as sodium ethyl diamine triacetate (EDTA), ineffective cost of chelants, much loss of chelants due to their coordination with Ca^{2+} , Mg^{2+} and Fe^{3+} in soils, and difficulty in recycling the flushing agents (Evangelou et al. 2007).

Anionic and nonionic surfactant usually form mixed-micelle aggregates that frequently exhibit properties remarkably different from those of the individual components (Rosen 1989, Zhao et al. 2005), in which the anionic one is capable to remove cationic heavy metals from soils through ion exchange and the nonionic one to desorb hydrophobic organic compounds due to its high solubilization capability. However, there have been few studies on simultaneous removal of both heavy metals and organic contaminants from soils using anionic-nonionic surfactants, as far as our knowledge concerns.

In this paper, copper (II) (Cu), phenanthrene (Phen), sodium dodecyl benzene sulfonate (SDBS) and octyl phenol polyoxyethylene ether (TX100) were selected as the representatives of heavy metals, hydrophobic organic pollu-

tants, anionic surfactants and nonionic surfactants, respectively. The comparison on batch washing of Cu-Phen co-contaminants from loess soil using single and mixed surfactants was conducted. A preliminary discussion on the mechanisms in washing process was made. The results could provide an implication for the remediation of soils co-contaminated by heavy metals and organic compounds.

Materials and Method

Chemicals

SDBS ($\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$; molar weight $348.48 \text{ g}\cdot\text{mol}^{-1}$; critical micellar concentration, CMC $963.2 \text{ mg}\cdot\text{L}^{-1}$, 25°C) with analytical grade was purchased from Laiyang Chemical Company, China. TX100 ($\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{9.5}\text{OH}$; molar weight $625 \text{ g}\cdot\text{mol}^{-1}$; CMC $167.4 \text{ mg}\cdot\text{L}^{-1}$, 25°C) was obtained from Acros Organics, USA and used as received. Phenanthrene ($\text{C}_{14}\text{H}_{10}$; molar weight $178.22 \text{ g}\cdot\text{mol}^{-1}$; water solubility $1.18 \text{ mg}\cdot\text{L}^{-1}$, 25°C) with analytical grade was obtained from Aldrich Chemical Company, USA. $\text{Cu}(\text{NO}_3)_2$ with analytical grade was bought from Tianjin Chemical Institute, China. Deionised water was used in all experiments.

Soil Preparation

A vadose zone loess soil (0-20 cm) sampled from Lanzhou, China, was airdried and sieved through a 0.28-mm sieve. The soil has a pH value of 8.14 and organic matter of 0.60%. The soil was spiked with Phen in acetone and then $\text{Cu}(\text{NO}_3)_2$ in water. The slurry was mixed homogeneously. The solvents were evaporated under hood, and the spiked soils with Phen and Cu were mixed and homogenized. The initial concentrations of contaminants were 200 mg Phen/kg soil and 2217.6 mg Cu/kg soil, respectively.

Washing Procedure

SDBS, TX100 and mixed SDBS-TX100 solutions were prepared with the total of 100, 200, 500, 1000, 2000, 3000 and 5000 mg/L concentrations, in which the mass ratios of SDBS to TX100 in the mixed surfactant solutions were kept as 1:1, 1:3 and 3:1, respectively. Hydrochloric acid and sodium hydroxide were used to adjust the pH value of solution as 7. The desorptions of Cu and Phen from simulated contaminated soils were measured with batch experiments. A series of 20 mL of surfactant solution and 2.0 g of contaminated soil were placed into 50-mL flasks with taps. 0.1 mL of 100 mg/L NaN_3 was added to inhibit microbial growth in all samples. The flasks were subsequently shaken at 25°C on a reciprocating shaker (CHA-S Shaker, Jintan Danyang Instrumental Company, China) at 120 rpm for 24 h. After shaking, the suspensions were centrifuged at 3000 rpm for 30 min. Then the supernatants were pipetted, diluted and analyzed.

Analytical Method

The concentration of Phen was determined on spectrophotometer (Model 752, Shanghai Spectrum Instrumental Company, China) with 1.0 cm quartz cell at 248 nm. The concentration of Cu was tested using sodium diethyldithiocarbamate spectrophotometric method at 440 nm (China EPA, 2002). The removal rate of contaminant was calculated according to the difference between the ultimate concentration in aqueous phase and the initial concentration on solid phase of contaminant.

Results and Discussion

Washing Results by Surfactant

The plots of the removal efficiencies of contaminants versus the surfactant concentrations are shown in Fig. 1.

Fig. 1 (a) shows that the capability of single TX100 to desorb Cu and Phen was relatively high as compared with deionised water (i.e. surfactant concentration is zero). With the increase of TX100 concentration, the removal efficiencies of Phen and Cu increased to different extent. When the concentration of TX100 was less than 1000 mg/L, the removal efficiencies of contaminants increased slowly. When the concentration of TX100 was larger than 1000 mg/L, the desorptions of Phen and Cu were enhanced heavily, especially for Phen. When the concentration of TX100 was 5000 mg/L, the removal efficiency of Phen was up to 73.1%, which was 2 times as that of Cu. The capability of TX100 to desorb Phen was much larger than to desorb Cu. This is attributed to the different mechanisms

on organics and heavy metals desorption by nonionic surfactant (Rosen 1989, Pennell et al. 1997). In general, the organics are much easier to partition into the hydrophobic cores of micelles when the surfactant concentration is larger than its CMC. However, only weak coordination between heavy metal ions and oxygen atoms in the poly oxyethylene chains of nonionic surfactant. Thus, the effect of TX100 upon the removal of Phen was much greater than that of Cu.

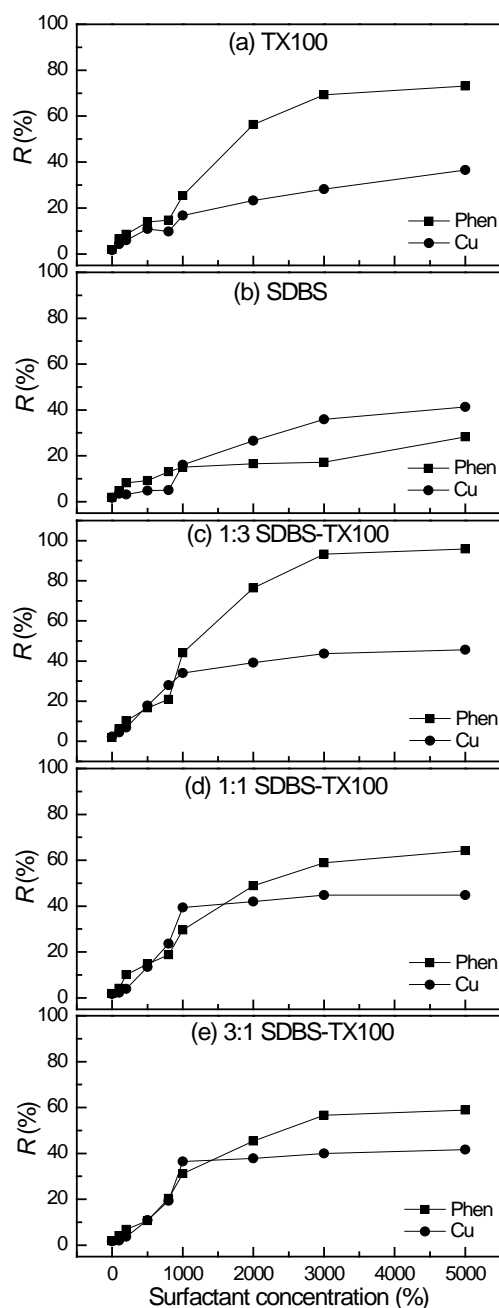


FIG. 1 PLOTS OF REMOVAL EFFICIENCIES (R) OF CONTAMINANTS VERSUS SURFACTANT CONCENTRATIONS

Fig. 1(b) shows the effects of SDBS concentration on the removal efficiencies of Phen and Cu. When the concentration of SDBS was less than or equal to 3000 mg/L, the removal efficiency of Phen increased slowly with SDBS concentration. When the concentration of SDBS was larger than 3000 mg/L, the increasing tendency of removal efficiency was much obvious. 28.3% of Phen was removed by 5000 mg/L of SDBS. As for Cu, the variation pattern of removal efficiency with SDBS concentration was somewhat different from that of Phen. When the SDBS concentration was less than 1000 mg/L, the rate of Cu desorption increased slowly with SDBS concentration increasing. However, when the SDBS concentration was larger than CMC (963.2 mg/L), the mechanisms of SDBS to desorb Cu was mainly micellar ion exchange. Thus, when the SDBS concentration was 5000 mg/L, the removed amount of Cu

could reach 41.3%, which was 1.5 times as that of Phen.

Fig. 1(c), (d) and (e) show the effects of the ratios and concentrations of mixed SDBS-TX100 on the removal efficiencies of Phen and Cu, respectively. It is observed that with the increase of initial concentration of surfactants, the tendency of desorption of both Phen and Cu improved. With the surfactant concentration less than 500 mg/L, the tendency was insignificant. However, it was much obvious with the concentrations of mixed surfactants larger than 500 mg/L. When the surfactant concentration was 5000 mg/L, both Phen and Cu desorption reached at the maximum extent. At this time, the desorbed amounts of Phen and Cu were 95.9 % and 45.7 % by 1:3 SDBS-TX100, 64.2% and 44.8% by 1:1 SDBS-TX100, and 58.9%, 41.6% by 3:1 SDBS-TX100, respectively. Fig. 1(c), (d) and (e) also show that in the entire testing range, the extent of desorption of Phen by anionic-nonionic surfactant solutions was much higher than that of Cu, showing a certain regularity. The removal efficiencies of Phen and Cu were associated with the different mass ratios of mixed surfactants. The more fraction of nonionic surfactant was used in the mixed systems, the more quantity of Phen and Cu was desorbed.

Comparison on Washing Results

Table 1 illustrates the desorptive results of Phen and Cu by single SDBS and TX100. With the increase of initial concentration of surfactant, the removal efficiencies of both Phen and Cu increased in a various degree. As for Phen, the desorption by TX100 was much larger than that by SDBS. For example, the removal efficiency of Phen by 5000 mg/L of TX100 was 2.6 times as that by 5000 mg/L of SDBS. As for Cu, the desorption by TX100 was slightly larger than that by SDBS with the concentration of surfactant less than 1000 mg/L while the desorption by SDBS was larger than that by TX100 with the concentration of surfactant larger than 1000 mg/L. At large, the clean up of Phen was better than that of Cu by TX100 and the desorption of Cu was better than Phen by SDBS respectively. Thus, for the remediation of co-contaminated soils in which the amounts of organics are dominated, the nonionic surfactant would be chosen. Otherwise, the anionic one would be better to be selected.

TABLE 1 COMPARISON ON WASHING EFFICIENCIES (%) OF CO-CONTAMINANTS BY SINGLE SURFACTANTS

Surfactant concentration (mg/L)	TX100		SDBS	
	Phen	Cu	Phen	Cu
0	1.89	1.66	1.89	1.66
100	6.53	3.87	4.82	3.50
200	8.54	4.24	8.14	3.13
500	13.9	5.16	9.25	4.79
800	14.7	5.34	13.0	4.97
1000	25.4	9.39	15.1	16.0
2000	56.3	23.2	16.5	26.5
3000	69.3	28.2	17.2	35.9
5000	73.1	36.5	28.3	41.3

Fig. 2 shows the relationship between the total washing efficiencies of co-contaminants and the concentrations of surfactants. In the whole range of surfactant concentrations, the total washing efficiencies of co-contaminants rose with the increase of initial concentration of surfactant. The processes could be divided into three stages in the different systems. When the surfactant concentration was low (<1000 mg/L) in the single SDBS and TX100 systems, with the surfactant concentration increasing, the total efficiencies changed slightly, especially in single SDBS system because the surfactant concentration had not reached its CMC. In the mixed surfactant systems, the participation of single non-ionic surfactant led to the reduction in CMC of anionic surfactant, thereby enhancing the washing effect by surfactants. As shown in Fig. 2, with the surfactant concentration less than 1000 mg/L, the mixed surfactants with the different ratios resulted in more desorption of co-contaminants. When the surfactant concentrations were between 1000 and 3000 mg/L, the single SDBS, TX100 and mixed SDBS-TX100s enhanced the desorption greatly. When the surfactant concentrations were larger than 3000 mg/L, the total efficiencies leveled off. It is obvious that the overall removal efficiencies of co-contaminants by mixed surfactant were larger than those by single surfactants.

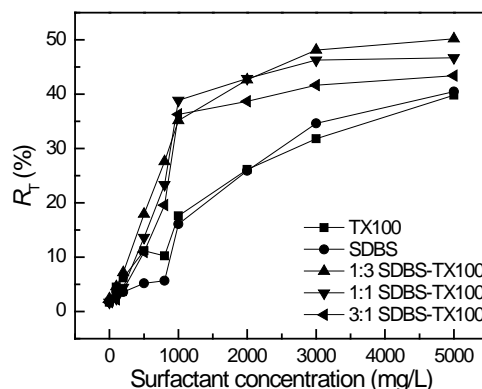


FIG. 2 RELATIONSHIP BETWEEN TOTAL WASHING EFFICIENCIES (R_T) OF CO-CONTAMINANTS AND SURFACTANT CONCENTRATION

Conclusions

The capability of TX100 to wash Phen out from soil was much greater than to Cu while SDBS was more capable to remove Cu efficiently. The mixed SDBS-TX100 exhibited significant capability to sweep the co-contaminants out from soil. The overall removal efficiencies of co-contaminants by mixed surfactant were larger than those by single surfactants. The results indicated that the mixed anionic-nonionic surfactants could be applied in the remediation of soils co-contaminated with organics and heavy metals.

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